Mathematical Analysis of the Energy and Relaxation of Grain Boundaries in Metals

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Abstract: **Systematical analytical description of the atomic density and energy on high-angle grain boundaries (GBs) is performed by the methods of molecular statics in reciprocal space. The multilayer oscillatory relaxation profile in the core region of tilt symmetric twin boundaries was found. It was found that the non-monotonic relaxation near the core of the GB is accompanied by the excess internal energy with the distance from the Σ3 {111} <110> incoherent tilt twin boundary. The displacements normal to the GB in the {211} and {110} general type boundaries correspond to the vast majority of the grain-boundary expansion taken up right at the boundary plane. In the case of the {211} GB there are oscillations in the normal displacements that decay exponentially away from the GB. At the {110} general boundary most of the dilatation is again taken up at the GB, but there are no oscillations in the normal displacements.**

Keywords: Mathematical Simulation; Molecular Statics; Grain Boundaries; Elastic Strain; Tungsten

I. INTRODUCTION

Physical properties of polycrystalline materials are determined to a great extent by the structure and properties of grain boundaries (GBs) [1]. Under usual conditions, polycrystals are found to rupture preferentially along their GBs due to the reduced cohesion of adjacent grains at GBs. At the same time, recent nanocrystalline structural materials demonstrate a wide diversity of exceptional mechanical properties due to the phenomenon of ultrafine grain refinement related to an increase in the density of GB network. Before the micromechanisms of this phenomenon can be understood, a detailed knowledge of the basic structural properties of GBs is required. In recent years, because of the experimental difficulties in measuring the atomic structure and mechanical characteristics of individual grain boundaries, a lot of effort has been put into atomic-scale simulating GBs focused on consideration of the structural and energetic characteristics of GBs. The expansion of the field of application of mathematical simulation of internal interfaces, in particular, due to the development of new approaches to the description of interatomic interactions. Thus, the calculation of the energy characteristics of grain boundaries and their configurations in terms of the model of rigid-body relaxation, performed in reciprocal space, makes it possible in a number of cases to analytically describe the dependence of the grain-boundary energy on their structure in the whole 5*D* space of macroscopic degrees of freedom of grain boundaries [1-3]. Despite the fact that this model ignores the atom-by-atom relaxation at grain boundaries, it permits one to quantitatively determine some structural parameters of boundaries that control their adhesion properties and the resistance to brittle intergranular fracture [2, 3].

The configurations and the energy parameters of symmetrical grain boundaries can be determined within the model of rigid-body displacements of atomic planes and can be performed in reciprocal space on the basis of a Fourier transform of empirical pair [1,3] or screened electrostatic [2] potentials. However, the investigation of the structure of grain boundaries using analytical relationships obtained in the approximation of pairwise Lennard-Jones potentials [1,3] is difficult in view of the divergence of the Fourier transform of the interatomic potential at small distances between atomic planes. Therefore, the use of the analytic model [3] is restricted to analyzing structure-insensitive types of grain boundaries, i.e., to incommensurate boundaries. In terms of the model of rigid-body relaxation with the use of screened electrostatic potentials [2], one can calculate only the structure-sensitive part of the energy of interaction of adjacent crystallites, i.e., the grain-boundary analog of the Ewald energy. In this work, the technique of simulation in reciprocal space is applied to analyze a local grain boundary dilatation, which determines grain boundary energy.

Most studies of grain boundary structure have focused on face-centered cubic materials, which form the coincident site lattices (CSL) (see e.g. Ref. 1). In spite of the technological importance of body-centered cubic (bcc) refractory metals, only few facts are known about atomic structure of high-angle grain boundaries. We studied the low-Σ <110> tilt and twist grain boundaries There Σ is the inverse density of coinciding sites. Due to their unusual properties, grain boundaries with low-Σ coincidence site lattices, in particular Σ3 boundaries play a special role in the grain boundary engineering.

II. MODEL AND METHODS

The most known interatomic potentials for bcc metals are sufficiently short range so that large-scale computer simulations can be implementing. During performing large simulation in real space, this reduces the time-consuming calculations; however, it does eliminate long range information which may be critical to reproducing certain features of the fine-structure of grain boundaries in metals. Because the change in electron density at the grain boundaries is small compared with, for example, a free surface, the Finnis-Sinclair and more sophisticated embedded atom potentials may be replaced quite acceptably by their effective pair potentials [1]. The GB structures in tungsten derived from an embedded atom model using the reciprocal space variational method agree with those results on the basis of a pair potential model. The empirical pair potentials should be identified with the effective pair potential of the embedded atom theory. The analysis in reciprocal space of the interaction between parallel planar atomic nets [2-4] includes determination of the two-dimensional Fourier transform of the

potential by the integrating extended over all two-dimensional space. In analytical treatment has no need to limit the range of the pair potential by forcing it to vanish at relatively small separations. We used an effective Morse potential for tungsten [1], based on fitting perfect crystal lattice properties.

Atomistic computer simulations were performed using molecular statics with Morse long-range potential. The thickness of the grain boundary interface model is taken as 30-50 crystallographic planes. Most methodical details of the calculation of the atomic configuration of the grain boundaries were described elsewhere [5, 6]. The Sutton version [3] of the variational calculation method in the reciprocal space is applied. The relaxed structure corresponds to a free of macroscopic stresses bicrystal. The relaxed configuration of the calculation block is determined by the molecular statics method by minimizing the energy, including the dilatation deformation with respect to the grain translations in the boundary plane and the local individual displacements of the atomic planes. The first stage of relaxation was rigid-body shift of the grains. After that, plane-by-plane relaxation was done. The GB energy was obtained by subtracting the internal energy of perfect bicrystals from the energy of the simulation block.

The energy minimization was carried out using the conjugate gradient method. To obtain an analytical expression for the energy of interface, the effective pair potential was used in form

$$v(r) = \sum_p D_p \exp(-\beta_p r), \quad (1)$$

where D_p and β_p are adjustable parameters, r is the distance between atoms. The potential parameters for W are: D_p = 8277 and -181.1 eV, β_p = 2.823 and 1.412 Å^{-1} for p = 1 and 2, respectively.

The energy of the system is represented by a sum of pair interactions of atoms in j and k planar atomic layers. Within each plane parallel to the grain boundary, we use the orthogonal coordinate systems x-y. To Let the lattice sites in these layers be denoted by the sets $\{\vec{X}^j\}$ and $\{\vec{X}^k\}$ and sets of the reciprocal lattice vectors are $\{\vec{G}^j\}$ and $\{\vec{G}^k\}$. The energy of interaction between two atomic layers per unit area may be written as

$$E_{jk} = \frac{1}{A_j A_k} \sum_{\vec{G}^c} \tilde{v}(\vec{G}^c, z_{jk}) \exp(i\vec{G}^c \cdot \vec{T}_{jk}), \quad (2)$$

where A_j and A_k are the areas of the primitive unit cells, z_{jk} is the separation between the lattices, $\vec{G}^c$ is a common reciprocal lattice vector, $\vec{T}_{jk}$ denotes an arbitrary relative translation, $\tilde{v}$ is two-dimensional Fourier transform of the pair-wise potential. For an effective potential in form (1) Fourier transform can be obtained in a closed form [6]:

$$\tilde{v}(G, z_{jk}) = 2\pi \sum_p \frac{\beta_p D_p}{(\beta_p^2 + G^2)^{3/2}} (1 + z_{jk}\sqrt{\beta_p^2 + G^2}) \exp(-z_{jk}\sqrt{\beta_p^2 + G^2}). \quad (3)$$

In order to compute the total energy of the pair-wise atomic interaction W a lattice summation must be performed. The lattice periods in the x and y directions are a_x, a_y and $|\vec{G}| = \sqrt{g_{xl}^2 + g_{ym}^2}$, where $g_{xl} = \frac{2\pi l}{a_x}$, $g_{ym} = \frac{2\pi m}{a_y}$ and l, m are summation indices locating points in the planar reciprocal lattice. Here a is the parameter of three-dimensional lattice. The module of the relative translation may be expressed as $|\vec{T}_{jk}| = \sqrt{T_{xjk}^2 + T_{yjk}^2}$.

Then, the energy of interaction can be written as

$$W = \pi\sigma^2 \sum_j \sum_{k(\neq j)} \sum_{lm} \sum_p \frac{\beta_p D_p}{q_{plm}^3} (1 + q_{plm}|z_{jk}|) \exp(-q_{plm}|z_{jk}|) \cos(g_{xl} T_{xjk}) \cos(g_{ym} T_{yjk}), \quad (4)$$

where $q_{plm} = \sqrt{\beta_p^2 + g_{xl}^2 + g_{ym}^2}$ and σ is the planar atomic density.

The convergence of the series for close-packed atomic planes is high and the method of simulation in reciprocal space is computationally efficient.

III. RESULTS AND DISCUSSION

A. Incoherent CSL Boundary

As it shown in Fig. 1 a, the atoms at the Σ3 {111} <110> tilt GB are initially located according to their positions in the coinciding-site lattice. Figure 1 b shows the atomic structures of this incoherent boundary after relaxation.

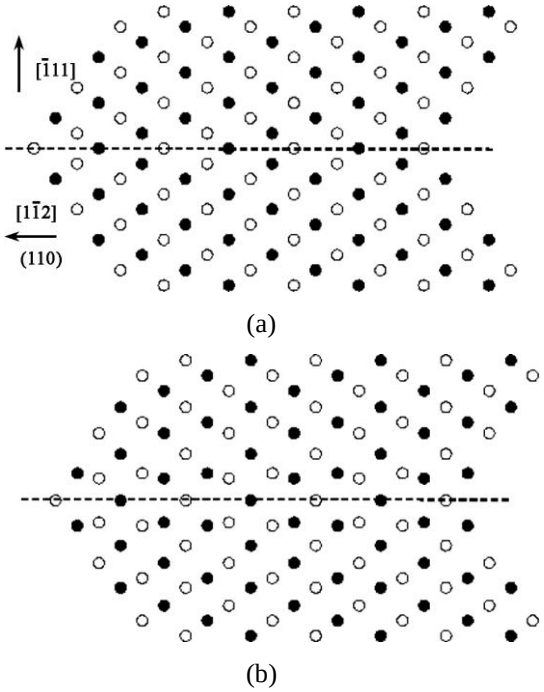

Fig. 1 Atomic structure of the Σ3 {111} <110> incoherent grain boundary in tungsten (a) before and (b) after relaxation

The solid and open circles are correspondent to atomic configurations of two neighboring monoatomic layers. The energy of the incoherent twin boundary corresponding to the atomic positions specified by the coinciding-site lattice and by relaxed models is equal to 19.7 and 3.2 J/m^2. The relaxed structure is characterized by the presence of dilatation perpendicular to the grain boundary with subsequent compression. It is found that the rigid displacement of the neighboring grains at the boundary along the [110] direction

is absent. It was ensured that the obtained atomic configuration in the relaxed region was completely unaffected by the free surfaces at the ends of the computational cell.

Fig. 2 shows the oscillatory relaxation profile near the core of the change in the excess internal energy with the distance from the incoherent twin boundary in the relaxed state.

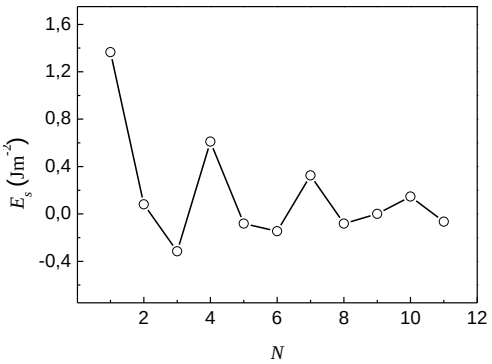

Fig. 2 The excess energy of {111} atomic layers near the incoherent twin boundary vs the number of atomic layer

B. General Twist Boundaries

The success of the variational calculations in the reciprocal space is that they correctly predict the trends for general GBs in the incommensurate limit. In the present paper, this technique is applied to symmetrical high-angle twist boundaries. Computations of twist boundaries provided insight into the nature of disordered configurations at general grain boundaries. In the model of a 'general twist grain boundary', all atomic interactions across the GB are assumed to be entirely random [1]. The energy of the GB properties is thus assumed to be independent of both the translations parallel to the GB and twist angle with a consequent reduction of the degrees of freedom to only the three associated with the GB plane and the GB expansion. Local configurations of twist boundaries can be regarded as models of local disordered configurations of general grain boundaries.

In the present application of the random GB model, full relaxation of the interplanar spacings on both sides of the GB plane will be included; in contrast to earlier work [1] in which only a volume expansion immediately at the GB, but no relaxation of the interplanar spacings away from the GB was permitted, and in which the surfaces are therefore unrelaxed. Such a boundary is an incommensurate interface. i.e., an interface in which the translation vectors of the adjoining crystal lattices in each direction within the interface are irrational multiples of each other. The GBs are not a CSL, i.e., does not have a finite volume or surface density of coincidence sites or a repeating cell.

These low index twist boundaries are singular with respect to a tilt angle, but in the incommensurate limit, they are general with respect to a twist angle.

Figure 3 shows the displacements normal to the GB in the fully relaxed {211} and {110} general twist boundaries ($\Sigma = \infty$). The vast majority of the grain-boundary expansion is taken up right at the boundary plane. In the case of the {211} GB there are oscillations in the normal displacements that decay exponentially away from the GB. In the case of the {110} general boundary most of the dilatation is again taken up at the GB, and there are no oscillations in the normal displacements. This boundary is free of stress at long range, in agreement with the assumptions of the analytic model of general GBs [1].

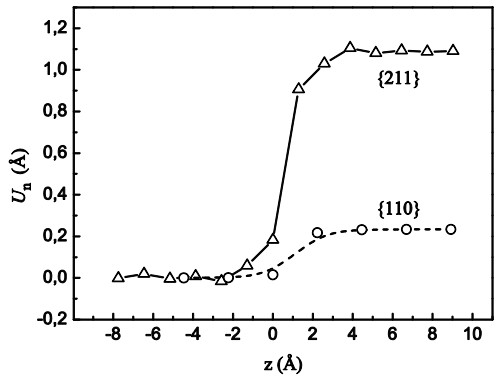

Fig. 3 Normal atomic displacements near the {211} and {110} general twist boundaries in tungsten, obtained by atomistic relaxation. The boundary plane is between layers 0 and 1; most of the GB dilatation is taken up between these layers

Analysis of the features of the stress field in the neighborhood of symmetrical twin and grain boundaries [7,8] allowed to replace the complex pattern of interaction of adjacent crystallites by periodic rows of parallel line forces for describing the strain field.

Linearly distributed forces are localized along the <111> directions, which have the maximum packing density at the twin boundary and are characterized by an increased stress level (up to 0.1 μ). Here the adjacent crystallites are treated as elastic continua bounded by the plane of the surface. The distance L between the lines of application of the forces along the x axis for this type of boundary is equal to the lattice period in the direction normal to the axis of misorientation. The forces P_z, uniformly distributed along the misorientation axis y, are directed along the z axis, normal to the boundary.

A line of P_y acting on a flat surface bounding an elastic half space results in the strain field in grains determined by [9]

$$\varepsilon_{xx} = \frac{2P_y(1+\sigma)}{\pi \cdot E} \cdot \frac{y}{x^2+y^2} \cdot \left(\sigma - \frac{x^2}{x^2+y^2}\right), \tag{5}$$

$$\varepsilon_{yy} = \frac{2P_y(1+\sigma)}{\pi \cdot E} \cdot \frac{y}{x^2+y^2} \cdot \left(\sigma - \frac{y^2}{x^2+y^2}\right), \tag{6}$$

$$\varepsilon_{zz} = \varepsilon_{xz} = \varepsilon_{yz} = 0, \tag{7}$$

where σ is Poisson's ratio, and E is Young's modulus. The displacement field associated with the system of parallel linear forces P_y can be found via a straightforward integration of Eq. 1 in the same manner as that of an array of lattice dislocations [7]:

$$U_y = \frac{P_y(1+\nu)}{2\pi \cdot E} \cdot \left\{ \begin{matrix} Y\left[\dfrac{\sinh(Y)}{\cosh(Y)-\cos(X)} - 2\nu + 1\right] \\ -2(1-\nu)\ln\left[\cosh(Y)-\cos(X)\right] \end{matrix} \right\}, \tag{8}$$

where $X = 2\pi x / L$ $Y = 2\pi y / L$. The force spacing L is equal to the GB interledge spacing.

Figure 4 shows the relaxed interlayer strain perpendicular to the boundary with an oscillatory behavior with a fast decaying profile with increasing number of atomic plane (111).

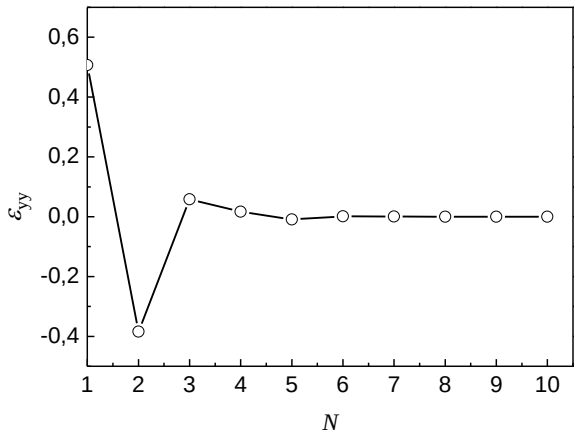

Fig. 4 Oscillatory behavior of interlayer strain perpendicular to the boundary with a fast decaying profile

By means of Hooke's law, one can express the amount of work per unit volume, or strain energy per unit volume *E* as a function of the strain only:

$$E = \frac{1}{2E}\left(\sigma_{xx}^2 + \sigma_{yy}^2\right) - \frac{\nu}{E}\cdot\sigma_{xx}\cdot\sigma_{yy} \qquad (9)$$

The total strain energy of a monolayer E_s^{el} of deformed elastic body is equal to Ed_{hkl}.

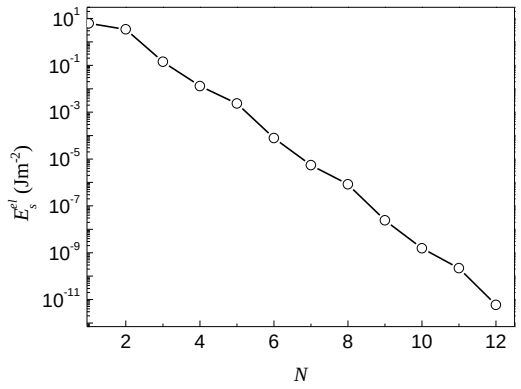

Fig. 5 The strain energy of a monolayer of deformed elastic body near the Σ3 {111} <110> tilt GB

Figure 5 shows a dependence of the total strain energy of a tungsten monoatomic layer near the Σ3 {111} <110> tilt GB. But in this case, the elastic energy decays exponentially into the bulk solid and has a periodic structure in the direction parallel to the boundary plane. The oscillation periods of the dependence of the excess energy of {111} atomic layers near the incoherent twin boundary on the number of atomic layer (Fig. 2) and the modulation periods of E_s^{el} coincide. However, as it follows from the form Fig. 5 the strain energy per monolayer is always positive and the rate of decay is substantially higher.

IV. CONCLUSION

We have presented elastic analysis for the energy and relaxation of GBs. The analytical model was then employed to determine the strain and elastic energy associated with the GB relaxation. It was found that the non-monotonic relaxation near the core of the GB is accompanied by the excess internal energy with the distance from the Σ3 {111} <110> incoherent tilt twin boundary. The displacements normal to the GB in the fully relaxed {211} and {110} general twist boundaries correspond to the vast majority of the grain-boundary expansion taken up right at the boundary plane. In the case of the {211} GB there are oscillations in the normal displacements that decay exponentially away from the GB. In the case of the {110} general boundary most of the dilatation is again taken up at the GB, and there are no oscillations in the normal displacements. This boundary is free of stress at long range, in agreement with the assumptions of the analytic model of general GBs.

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